# Comparative Behavior of Titanium and Zirconium in Hydrofluoric–Nitric Acid Pickling Solutions ☆

*E.M.M. Sutter, F. Hlawka, and A. Cornet**

## ABSTRACT

*The different behavior of titanium and zirconium in HF–$HNO_3$ pickling solutions has been studied using electrochemical methods and Raman spectrometry. In each case, the depleting of the solutions during a pickling experiment could be correlated with the consumption of HF to form metal oxo or oxofluoro complexes. However, the mechanism of metal dissolution is quite different for the two metals. The titanium dissolution process in such solutions can be interpreted using a passivation model in which dissolution and passivation are two competing reactions at the surface of the bare metal. On the other hand, zirconium dissolution occurs through formation of an oxide film with ionic diffusion through the film being a rate-determining step. The particular role of strong acid added to the HF solution for pickling of titanium and zirconium is also discussed.*

*KEY WORDS: corrosion, hydrofluoric–nitric acid, pickling, Raman spectrometry, titanium, zirconium*

## INTRODUCTION

Titanium, zirconium, and their alloys are widely used in industries employing corrosion-resistant metals. Indeed, both metals exhibit excellent corrosion resistance in many aggressive media because of the formation of a stable, protective, passive film of $TiO_2$ or $ZrO_2$.

Titanium and zirconium dissolve in hydrofluoric acid solutions, with the formation of hydride at the metal surface accompanied by embrittlement. Thus the industrial pickling of both metals is usually carried out in an aqueous mixture of nitric and hydrofluoric acids.

Nevertheless, titanium and zirconium behave quite differently in a number of aggressive media. In general, zirconium is less resistant than titanium in oxidizing halide media, but it is superior to titanium in resistance in non-oxidizing acids ($H_2SO_4$, HCl) and in alkalis. Even in HF–$HNO_3$ solutions the electrochemical behavior is different for titanium and zirconium, involving different mechanisms of dissolution.

In this work, weight-loss data are reported for both metals in HF–$HNO_3$ solutions. The electrochemical behavior of the metals during pickling is compared in fresh and depleted HF–$HNO_3$ solutions.

A Raman spectrometric study of the fresh and depleted pickling solutions was made. Since the Raman effect occurs by scattering of light from polarizable bonds, important information can be obtained about molecular species present in the solution. Based on these results, corrosion mechanisms are discussed for each metal and the different behavior during dissolution is interpreted. The better understanding of the dissolution process and the nature of metal species in HF–$HNO_3$ solution will allow an efficacious regeneration of the spent pickling solutions.

## EXPERIMENTAL

Electrochemical experiments were performed using a Tacussel[1] potentiokinetic device. Current versus potential curves were recorded at a scan rate between 1 and 10 mV/s using a saturated calomel electrode (SCE) as reference and platinum as the counter electrode.

Working electrodes were cut from commercially pure Ti and Zr bars obtained from CEZUS[2] in the annealed condition and containing the following minor impurities: for titanium, 0.15% O, 0.09% Fe, 0.19% C, 0.015% N, 0.014% Cu; for zirconium, 0.14% O, 0.15% Fe, 0.03% C, 0.01% Hf, 0.008% N.

These disk electrodes, 15 mm in diameter, were mounted in a chemically inert resin or in a polytetrafluoroethylene (PTFE [Teflon†]) holder so that only one face was exposed to the test solution. Samples of Ti and Zr were mechanically polished (grade 600), rinsed, then immersed for a few minutes at 20°C in the electrochemical PTFE cell containing the HF–$HNO_3$ mixture before recording the potentiokinetic curves. All solutions were prepared from ultra pure commercially available reagents. For weight-loss measurements, 3- to 4-mm-thick Ti and Zr disks were cut from the same samples. During weight-loss and electrochemical measurements, the solutions were magnetically stirred at the highest available stirring rate so that all experiments were conducted under comparable hydrodynamic conditions.

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†Trade name.


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Raman spectrometry was performed using the 488-nm spectral line of a Spectra Physics[3] argon laser, on a Coderg[4] PH 1 spectrometer with a plexiglass cell. A schematic representation of the experimental set up is shown in Figure 1.

## RESULTS AND DISCUSSION

When a Ti or a Zr sample was immersed in a typical $HF–HNO_3$ pickling solution (1.1 M HF–4.5 M $HNO_3$), the dissolution rate progressively decreased (Figure 2) and the pickling solutions became less effective with time, probably as a result of the consumption of the hydrofluoric acid. Thus the behavior of Ti and Zr in fresh solutions has to be distinguished from their behavior in depleted pickling baths.

### *Behavior of Ti and Zr in Fresh $HF–HNO_3$ Solutions*

*Influence of the Acid Concentrations* — For pickling of Ti in an $HF–HNO_3$ solution, the concentrations of the acids can be optimized to obtain a fast pickling rate without hydrogen pickup by the metal.[2] Even in the case of Zr, hydrogen pickup by the metal is avoided by the use of nitric acid and the resulting pickled Zr surface is shiny compared to the rough surface obtained in an HF solution without $HNO_3$. However, unlike that of Ti, the dissolution rate of Zr is quite independent of the nitric acid concentration.[2] In Table 1, the variations of the corrosion potential of Ti and Zr with varying nitric acid concentration are reported. With increasing concentration of $HNO_3$, the corrosion potential of Ti becomes more positive and shows a large potential shift. Thus, during a pickling experiment, $HNO_3$ behaves much like an oxidizer towards Ti and favors the formation of a passive film. On the contrary, the corrosion potential of Zr changes by only a small value when nitric acid concentration increases.

During anodization of the metals in a typical $HF–HNO_3$ solution, the potentiokinetic curve (Figure 3) is characteristic of a passive system in the case of Ti but of an active system for Zr, for which the curve shows a constant current plateau characteristic of a mass transfer process control. The value of i depends on the initial HF concentration according to the equation

$$i = k(HF) \qquad (1)$$

with k = 0.63 A/cm² L/mol at 20°C. Comparable values for k have been found by Meyer,[4,5] Smith and Hill,[6] or Vander Wall and Whitener.[3] Identical potentiokinetic curves can be obtained with Zr whether the solution is an $HF–HNO_3$ mixture or an $HF–H_2SO_4$ mixture with the same $[H^+]$ (Figure 4[a]). In either solution, the Zr surface is bright and shiny. On the contrary, when $HNO_3$ is replaced by $H_2O_2$ during pickling, Zr behaves in $HF–H_2O_2$ as it does in HF without $HNO_3$ (Figure 4[b]), and hydride formation is observed on the metal surface. Thus in the case of Zr, the acidic properties of $HNO_3$ are more important than its oxidizing properties. The role of the strong acid added to an HF solution is to increase $[H^+]$ irrespective of its oxidizing properties and to promote the formation of a film on the metal surface. These results are in agreement with Meyer's results.[4] In $HF–H_2SO_4$ solutions at various $[H^+]$, Meyer showed that the film thickness increases with increasing $[H^+]$, that $H^+$ is reduced during film formation, and that the rate of the cathodic reaction is first order with respect to $[H^+]$. Vander Wall and Whitener[3] concluded that $HNO_3$ is not an important factor in the dissolution step but only in the production of species not subject to precipitation as in an HF solution without $HNO_3$.

### *Behavior of Ti and Zr in Depleted $HF–HNO_3$*

The weight-loss data in Figure 2 show a decrease with time of the pickling rate of Ti and Zr. In the case of Ti, such a behavior has been interpreted[7,8] in terms of a modification of the pickling solution by consumption of HF to form soluble Ti complexes. Like Ti, Zr is well known[9,10] to form fluoride complexes easily in hydrofluoric acid solutions.

In Figure 5, the instantaneous dissolution rates $\Delta W/\Delta t$ calculated at every 10 minutes are plotted against the corresponding concentration of dissolved metal in the pickling solution. For both metals, when the amount of dissolved metal increases in the bath, the pickling rate decreases linearly until the concentration of dissolved metal reaches approximately 0.21 M for Ti and 0.11 M for Zr. At higher concentrations, the pickling rate decreases much more slowly and the saturation of the solution is reached for a metal concentration of about 0.58 M for Ti and 0.38 M for Zr. It can be mentioned that in a 1.1 M HF solution, the acid pickling solution becomes saturated for a dissolved metal concentration of

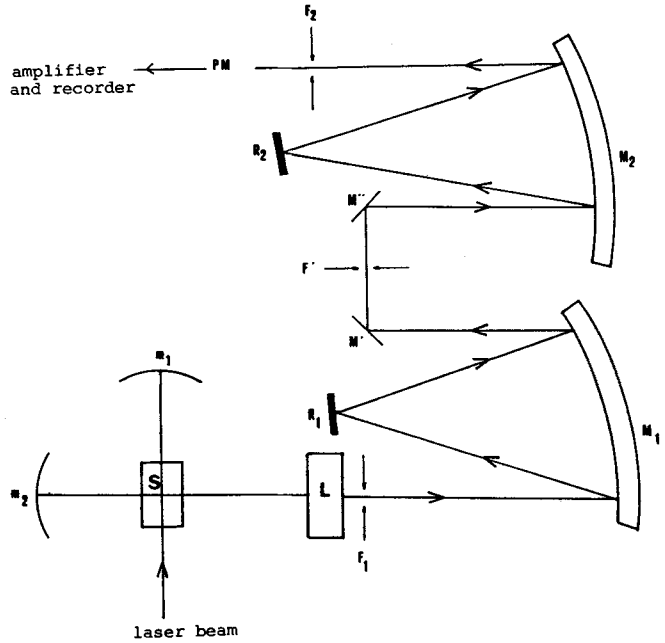



**FIGURE 1.** *Optical diagram of the Raman spectrometer. S: sample; $m_1$, $m_2$, M', M": mirrors; $M_1$, $M_2$: focusing mirrors; $F_1$, $F_2$, F': slits; L: lens; $R_1$, $R_2$: gratings; PM: photomultiplier.*

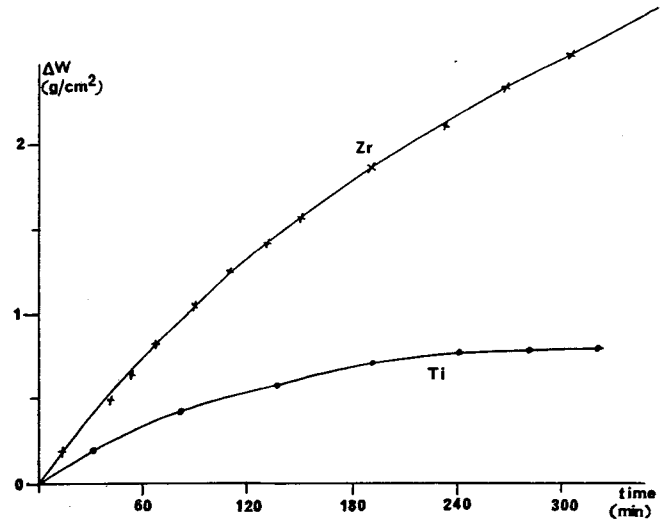



**FIGURE 2.** *Weight loss of metal samples in a 1.1 M HF–4.5 M $HNO_3$ solution.*

[3]Spectra Physics Inc., Laser Products Div., Mountain View, CA.

[4]DILOR, Lille, France.

**TABLE 1**
*Corrosion Potentials of Ti and Zr in Stirred HF–$HNO_3$ Solutions*

| Composition of the Solution | | Corrosion Potential ($mV_{SCE}$) | |
|---|---|---|---|
| HF (mol/L) | $HNO_3$ (mol/L) | Ti | Zr |
| 1.1 | 0 | −1026 active | −1100 active |
| 1.1 | 1.5 | −830 passivating | −1100 active current plateau |
| 1.1 | 3 | −750 passivating | −1050 active current plateau |
| 1.1 | 4.5 | −690 passivating | −1050 active current plateau |
| 1.1 | 6 | −300 passive | −1000 active current plateau |
| 1.1 | 7.5 | −200 passive | −1000 active current plateau |

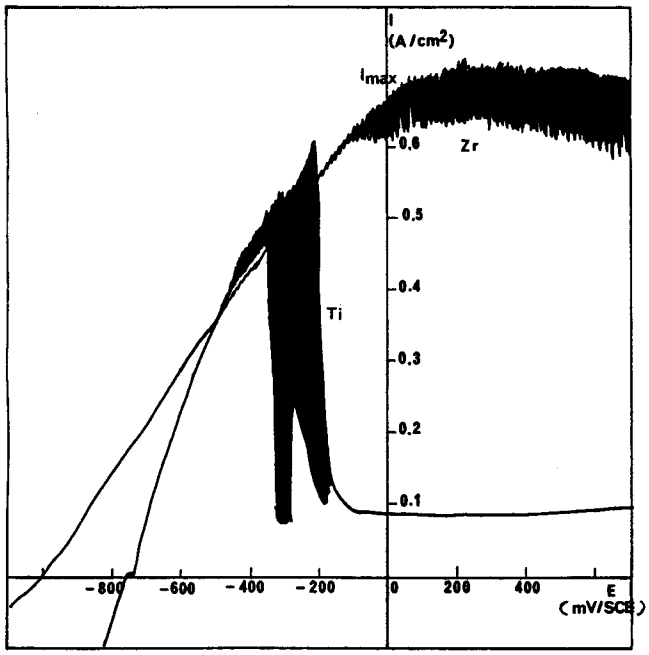



**FIGURE 3.** *Potentiokinetic polarization curve of Ti and Zr in a 1.1 M HF–4.5 M $HNO_3$ solution.*

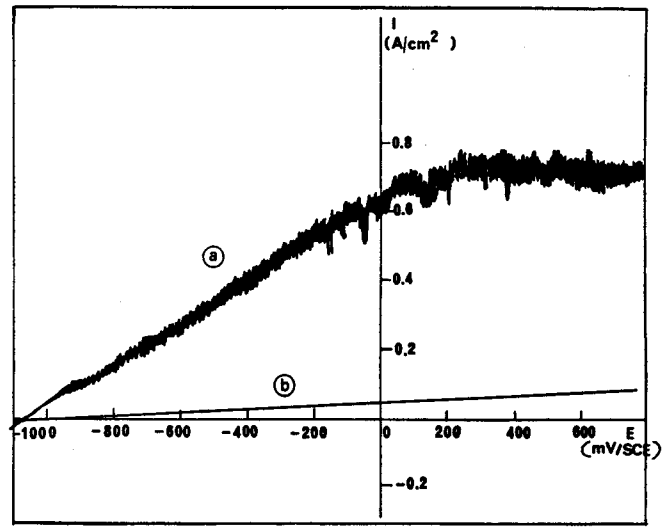



**FIGURE 4.** *Potentiokinetic polarization curves of Zr: (a) in a 1.1 M HF–2.2 M $H_2O_2$ solution, (b) in a 1.1 M HF–30 vol% $H_2O_2$ solution.*

0.37 and 0.27 M for Ti and Zr, respectively. These results are reported in Table 2 where corresponding $[HF]_{initial}/[metal]_{solution}$ are calculated for each metal concentration. Assuming during anodic polarization of Zr in HF–$HNO_3$ solutions with constant $HNO_3$ concentration, that the limiting current plateau $I_{max}$ is proportional to the concentration of undissociated HF, the concentration of consumed HF could be estimated.[4] For a few Zr concentrations, the ratios $[HF]_{consumed}/[Zr]_{solution}$ are also reported in Table 2. The variations of $I_{max}$ with $[Zr]_{solution}$ are plotted in Figure 6.

In the case of Ti, the potentiokinetic curves are given in Figure 7 for three dissolved metal concentrations. Initially, all the solutions contained 1.1 mol/L HF and 4.5 mol/L $HNO_3$. With increasing concentrations of Ti in the solution, the following changes occur: The activity peak is shifted towards more negative potentials, the critical current for passivation and the steady-state passive current decrease, and the corrosion potential is shifted toward more noble values.

Though for both metals the loss of efficiency of the aged pickling baths may be due to the consumption of hydrofluoric acid to form fluorocomplexes, the different potentiokinetic behavior of Ti and Zr shows that different dissolution mechanisms are involved.

## *Identification of Ti and Zr Complexes by Raman Spectrometry*

Since identification of the complexes formed during pickling of Ti and Zr in a 1.1 M HF–4.5 M $HNO_3$ solution would likely allow us to propose a dissolution mechanism, a Raman spectrometric study of depleted solutions has been performed for several $[HF]_{initial}/[metal]_{solution}$ ratios. The Raman technique is well suited to the investigation of this problem since the solutions are usually colorless or pale yellow and hydrofluoric acid does not give strong Raman lines of its own.

Figure 8(a) shows the reference Raman spectrum of a metal-free 1.1 M HF–4.5 M $HNO_3$ solution. All the vibrational frequencies can be attributed to the characteristic vibrations of nitric acid and nitrate ions.[11] Hydrofluoric acid does not show any vibrational band in the frequency range 300 to 1800 $cm^{-1}$.

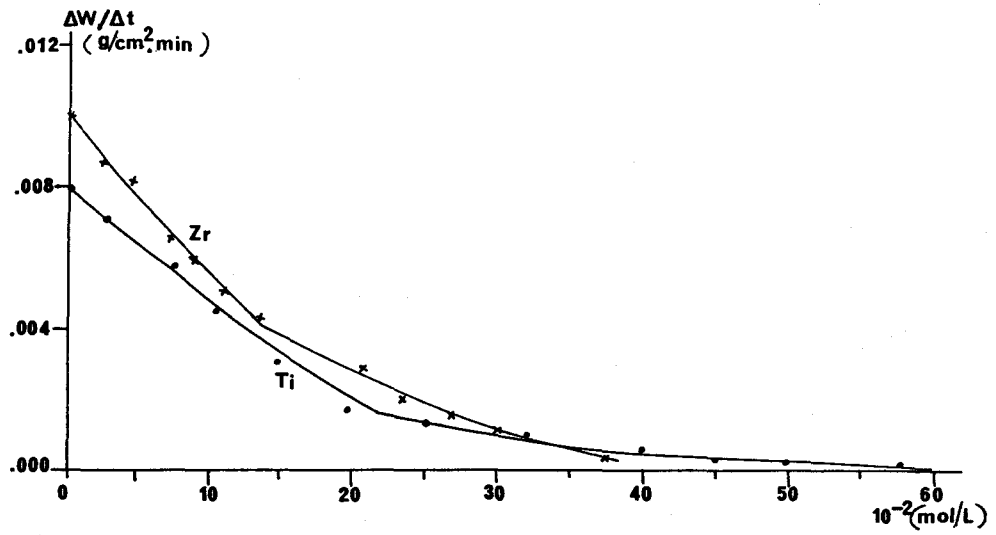



**FIGURE 5.** *Instanteous dissolution rate of Ti and Zr as a function of the dissolved metal content of the solution.*

**TABLE 2**
*Concentration of Dissolved Metal in Some Pickling Solutions*

| Nature of the Acid | Metal Concentration (mol/L) | Corresponding $[HF]_{initial}/[Ti]$ | Corresponding[A] $[HF]_{consumed}/[Zr]$ |
|---|---|---|---|
| 1.1 M HF | Ti 0.37 | 3.0 | |
| 1.1 M HF–<br>4.5 M $HNO_3$ | Ti 0.21<br>Ti 0.58 | 5.2<br>1.9 | |
| 1.1 M HF | Zr 0.27 | 4.1 | |
| 1.1 M HF–<br>4.5 M $HNO_3$ | Zr 0.11<br>Zr 0.38 | 10.0<br>2.9 | 5<br>2 |

[A]Calculated according to Reference 4.

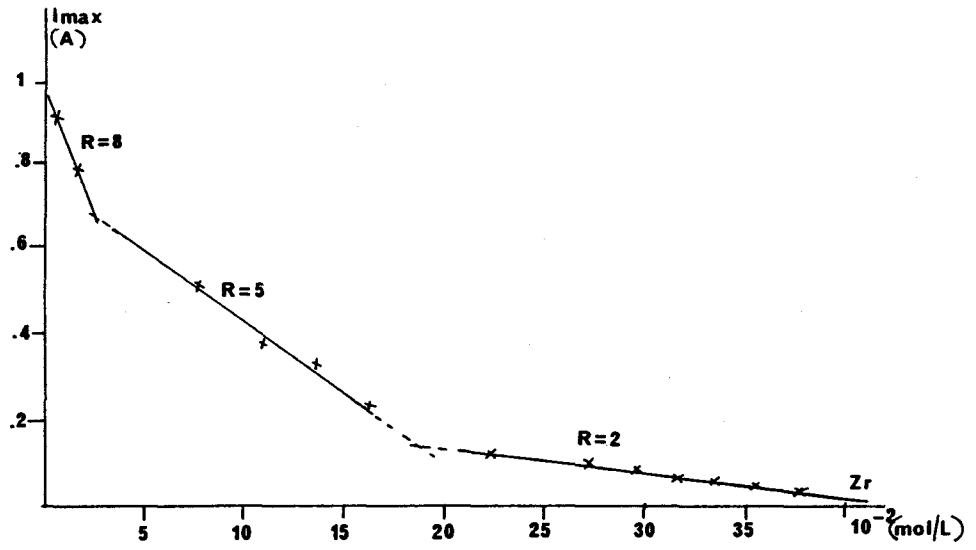



**FIGURE 6.** *Variation of $I_{max}$ with Zr content of the solution. $R = [HF]_{consumed}/[Zr]_{solution}$ calculated according to Reference 4.*

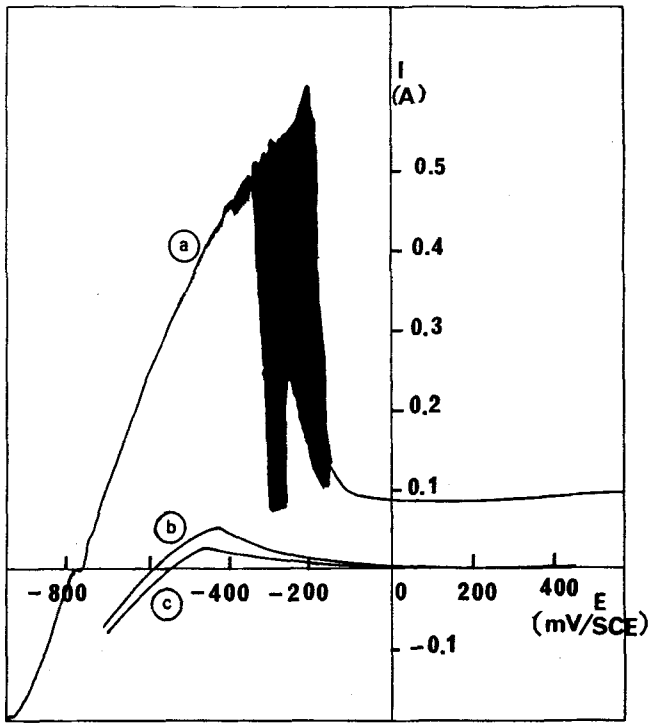



**FIGURE 7.** *Potentiokinetic polarization curves of freshly polished Ti electrodes immersed in various solutions: (a) 1.1 M HF–4.5 $HNO_3$ solution; (b) depleted solution "a" containing 0.21 mol/L Ti; (c) depleted solution "a" containing 0.42 mol/L Ti.*

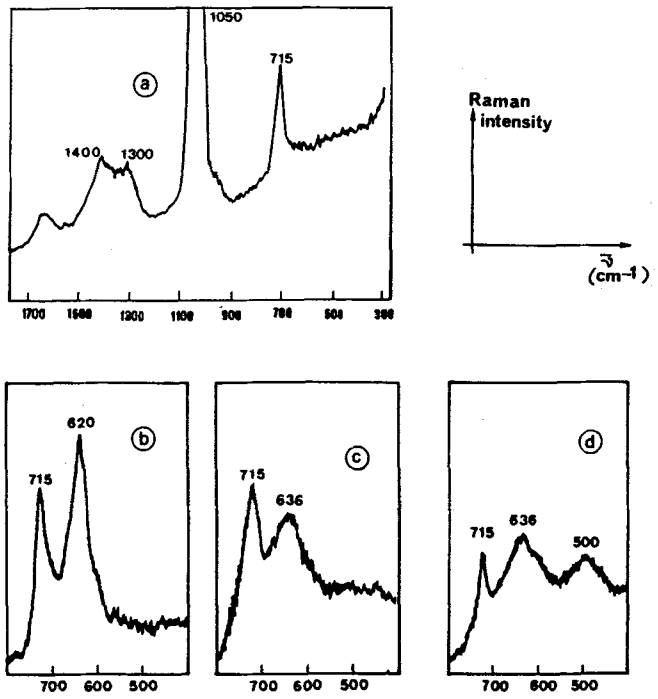
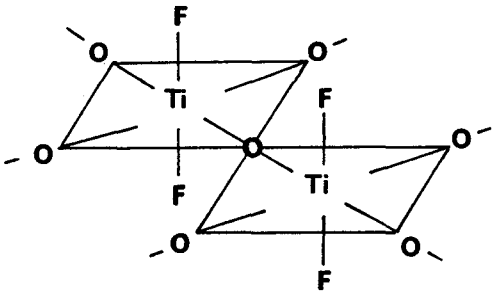



**FIGURE 8.** *Raman spectra of new, old, and depleted Ti pickling solutions: (a) 1.1 M HF–4.5 $HNO_3$ solution; (b) depleted solution "a" with 0.15 mol/L Ti; (c) solution "b" 3 days old; (d) depleted solution "a" with 0.35 mol/L Ti.*

In the case of Ti, a past study[7,8] showed that for $[HF]_{initial}/[Ti]_{solution} > 6$ and $[Ti]_{solution} > 0.06$ M, a new vibrational band appears at 620 $cm^{-1}$ (Figure 8[b]), which has been assigned to the totally symmetric stretching mode of the $TiF_6^{2-}$ ion. When this solution is aged (about 3 days), the 620-$cm^{-1}$ band becomes broad and is shifted to higher frequencies by about 20 $cm^{-1}$ (Figure 8[c]). This phenomenon has been assigned to a slow hydrolysis reaction leading to fluoride displacement by oxygen containing ligands, i.e.,

$$TiF_6^{2-} + 2H_2O \rightleftarrows [TiF_4OH{\cdot}H_2O]^- + HF + F^- \qquad (3)$$

Further, in pickling solutions in which the $[HF]/[Ti] \cong 3$ (Figure 8[d]), a new broad band appears at 500 $cm^{-1}$, which has been attributed to Ti–O–Ti bridges.[12] Oxofluoro or hydroxofluoro dimeric complexes are then probably formed[8] with a limiting stoichiometry for such species of [F]/[Ti] = 2.




The (HF)/(Ti) = 1.9 ratio determined by weight-loss measurements (Figure 5 and Table 2) for saturated HF–$HNO_3$ pickling solutions corroborates this hypothesis.

Similar experiments were performed for Zr at several $[HF]_{initial}/[Zr]_{solution}$ ratios and the following results were obtained: Below metal concentration of 0.2 M, no vibrational band was observed in the range 300 to 1000 $cm^{-1}$. For concentrations greater than 0.2 M Zr in solution, a vibrational band appeared at 550 $cm^{-1}$ (Figure 9[a]). This band is polarized and corresponds to a totally symmetric mode. When fresh HF is added to the same solution (2.26 mole HF added into 1.0 liter of solution), the 550 $cm^{-1}$ vibrational band is shifted to 580 $cm^{-1}$ (Figure 9[b]).

For a better assignment of the observed vibrational bands, some Raman experiments were performed on 1.1 M HF solutions without $HNO_3$ but with comparable $[HF]_{initial}/[Zr]$ ratios. Figures 9(c) and 9(d) show the Raman spectra of two HF solutions with initially 1.1 M HF concentration. For the solution containing approximately 0.16 mol/L Zr (Figure 9[c]), a sharp vibrational band is observed at 580 $cm^{-1}$. For the solution with about 0.20 mol/L Zr (Figure 9[d]), a vibrational doublet appears at 550 and 580 $cm^{-1}$. As observed before, when new HF was added later, the 550 $cm^{-1}$ band disappeared while the 580 $cm^{-1}$ band remained.

For the identification of the Zr complexes formed in hydrofluoric–nitric acid, little data exists in the literature, but the well-known [13] strong tendency of Zr towards hydrolysis involving complicated polynuclear equilibria could be implicated.The 580 $cm^{-1}$ vibration is generally attributed to the $\nu 1$(Zr – F) stretching of A1 symmetry of the $ZrF_6^{2-}$ anion. Vibrational assignments have been reported[14] for Raman spectra of $Cs_2ZrF_6$ and $Rb_2ZrF_6$ ($\nu 1$ = 579 and 588 $cm^{-1}$, respectively) and of solutions of $ZrO_2$ in 5 M HF ($\nu 1$ = 588 $cm^{-1}$).[15] The polymeric nature of such complexes has been shown. Each zirconium is surrounded by eight fluorine atoms and fluorine bridges exist between adjacent polyhedra.[14] In HF–$HNO_3$ solutions, the 550-$cm^{-1}$ band that appears for a relatively high metal concentration (0.3 mol/L, $[HF]_{initial}/[Zr] = 3.7$) may be compared with the 500 $cm^{-1}$ vibrational band of Ti[8] in like solutions and therefore can be attributed to vibration of Zr–O–Zr bridged species. For Zr, polynuclear ions are known to occur in solution of high acidity,[16] but the tendency to polymerize increases when acidity decrease below 2 M and when metal concentration increases. Thus the absence of well-defined vibrational bands for Zr concentrations below 0.2 mol/L is probably due to the absence of a well-defined species in solution and to the existence of a mixture of various monomeric or polymeric species of the type $(ZrO_xF_y)_n$ with a low degree of symmetry. When the $[HF]_{initial}/[Zr]$ ratio reaches the value 4, a well-defined species tends to form with a high degree of symmetry of the type $ZrO_2F_4^{2-}$.

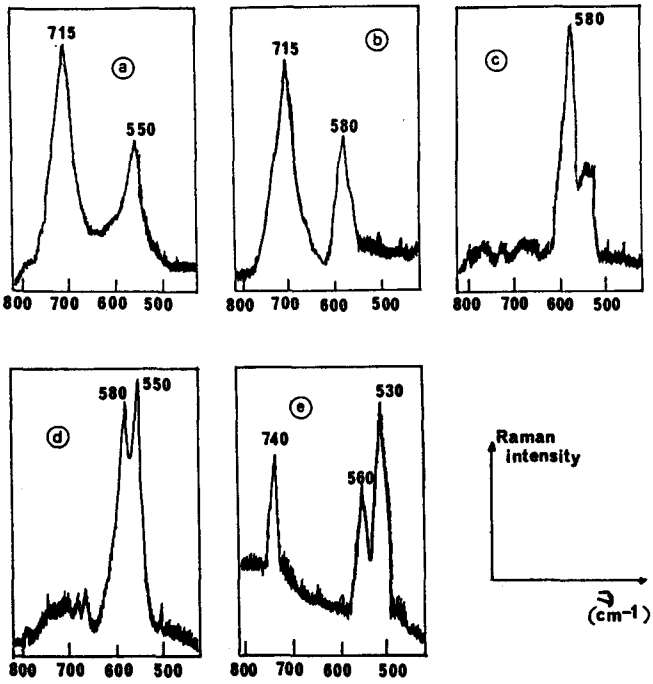



**FIGURE 9.** *Raman spectra of new and depleted Zr pickling solutions: (a) 1.1 M HF–4.5 $HNO_3$ mol/L Zr; (b) solution "a" with 2.2 mol/L HF added; (c) 1.1 M HF with 0.16 mol/L Zr; (d) 1.1 M HF with 0.20 mol/L Zr; (e) 1.1 M HF–4.5 $HNO_3$ saturated with Zr (approximately 0.69 mol/L).*

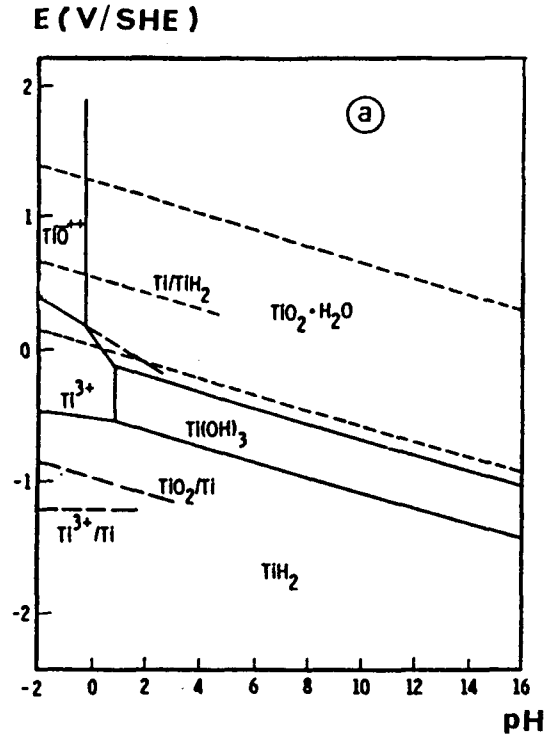
Figure 9(e) shows the Raman spectrum of the HF–$HNO_3$ solution saturated with 0.69 mol/L Zr (corresponding to an $[HF]_{initial}/[Zr]$ ratio of 1.6). The shift of the 715 $cm^{-1}$ $NO_3^-$ vibrational band to 740 $cm^{-1}$ may be attributed to the presence of Zr–$O_3N$ groups, by analogy[12] with the 750 $cm^{-1}$ vibrational band of $Zr(NO_3)_6^{2-}$ The splitting of the 550 $cm^{-1}$ band into two bands, at 530 and 565 $cm^{-1}$, tends support to the hypothesis of a partially modified environment of the bridged Zr–O–Zr groups.

## *Discussion*

Let us compare the potential–pH diagrams of Pourbaix[17] partially modified by Beck[18] for the two systems Ti–$H_2O$ and Zr–$H_2O$ (Figure 10[a] and 10[b], respectively). At the corrosion potential of Ti in a 1.1 M HF–4.5 M $HNO_3$ solution (−690 $mV_{SCE}$ or −445 $mV_{SHE}$), $Ti^{3+}$ should form spontaneously. On the other hand, at the corrosion potential of Zr in the same solution (−1000 $mV_{SCE}$ or −755 $mV_{SHE}$), $ZrO_2$ should be the most stable species. The following equations must be taken into account[17,18] (the standard potentials are given with respect to the standard hydrogen electrode):

$$\left.\begin{aligned} &Ti \rightleftarrows Ti^{3+} + 3e^- \\ &E_o = -1.21\ V \end{aligned}\right\} \qquad (1)$$

$$\left.\begin{aligned} &Ti^{3+} + 2H_2O \rightleftarrows TiO_2 + 4H^+ + e^- \\ &E_o = -0.30 - 0.236\ pH \end{aligned}\right\} \qquad (2)$$



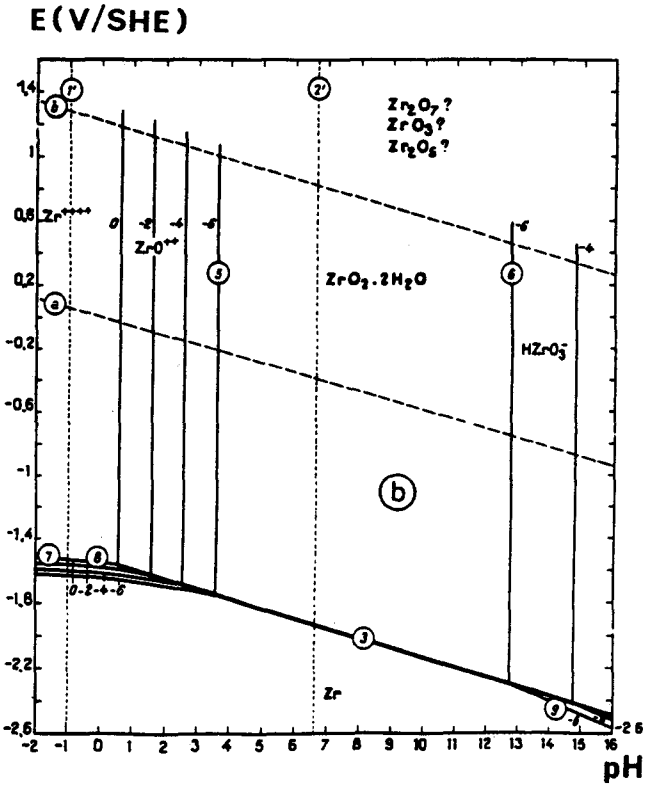




**FIGURE 10.** *E versus pH diagrams at 25°C: (a) for the Ti–$H_2O$ system, according to Reference 18; (b) for the Zr–$H_2O$ system, according to Reference 17.*

$$TiH_2 + 2H_2O \rightleftarrows TiO_2 + 6H^+ + 6e^- \qquad E_o = -0.47 - 0.059\ pH \qquad (3)$$

$$Zr + 2H_2O \rightleftarrows ZrO_2 + 4H^+ + 4e^- \qquad E_o = -1.553 - 0.0591\ pH \qquad (4)$$

This means that dissolution of Ti in an HF–$HNO_3$ pickling solution occurs at the surface of the bare metal, but dissolution of Zr proceeds through a $ZrO_2$ or $ZrO_2{\cdot}H_2O$ oxide film, and bare metal does not react directly with solvent. This hypothesis is corroborated by the potentiokinetic polarization curves (Figure 3 and Table 1). Ti is passivated in an HF–$HNO_3$ solution when the corrosion potential reaches the value $-300\ mV_{SCE}$. The most stable form is then $TiO_2$ or $TiO_2H_2O$ and the film formed at the surface of the metal is a protective film (low passive current). For the formation of this passive film, a kinetic model has been proposed[8] in which dissolution and passivation are two competing reactions, the most important parameters being the coverage of the metal surface by adsorbed $Ti^{3+}$ cations. If the surface coverage is low in $Ti^{3+}$ (low oxidation rate or high HF concentration), these cations are oxidized as soluble Ti fluorides according to the reaction:

$$Ti^{3+}_{ads} + 1/2\ HNO_3 + n\ HF \rightarrow TiF_n^{(n-4)-} + 1/2\ HNO_2 + (n-1)\ H^+ + 1/2\ H_2O \qquad (5)$$

If the surface coverage is high (high oxidation rate or low HF concentration), adsorbed $Ti^{3+}$ cations are oxidized as insoluble Ti oxide according to:

$$Ti^{3+}_{ads} + 1/2\ HNO_3 + 3/2\ H_2O \rightarrow TiO_2 + 1/2\ HNO_2 + 3H^+ \qquad (6)$$

or

$$Ti^{3+}_{ads} + 2H_2O \rightarrow TiO_2 + 4H^+ + e^- \qquad (7)$$

$HNO_3$ behaves in these reactions like an oxidizer. In such an active–passive transition model, the most important parameter is the metal surface coverage. This model has been used by many authors[19] for some other metals.

At the corrosion potential of Zr in a 1.1 M HF–4.5 M $HNO_3$ solution, Zr is already covered with an oxide film, but this film is not protective in HF solutions, and dissolution occurs through the film. The current plateau on the anodic polarization curve (Figure 3) involves the diffusion of ionic species through the film. Thus for a given HF concentration of the pickling bath, the oxidation rate of the metal is limited by the mass transfer rate through the oxide film. It may be noted that the I–E curve of Zr in HF without $HNO_3$ is a straight line identical to the curve on Figure 4(b), and no current plateau appears in the potential range studied.

In this case, no oxide film is present at the metal surface.

Our experimental results agree with those of other authors[3–5] and show that the dissolution rate of Zr is given by the equation

$$r = k_1\ [HF]_{initial} \qquad (8)$$

It is controlled by the rate of mass transfer of undissociated HF to the surface of the film and is potential independent. Such a behavior is understable if the potential at the oxide–solution interface stays constant as the overall potential between the metal and the solution is changed. The equilibrium

$$2H^+ + O^{2-}_{lattice} \rightleftarrows H_2O \quad (9)$$

will then determine the potential at the oxide–solution interface.[5]

The overall dissolution reaction of Zr in an HF–$HNO_3$ solution involves a complex mechanism that is the resultant of different reactions: At the metal–oxide interface, oxidation may occur providing $Zr^{4+}$ ions.[20] The rate of oxidation depends on the applied potential and on the presence of $H^+$ in solution, assuming that reduction of $H^+$ occurs through the oxide film by the electronic tunneling mechanism.[21] The particular role played by $H^+$ on the oxidation rate of the metal can be correlated with the incorporation of protons in the oxide film, as mentioned by Banter[22] for Zr and by Kover and Musselin[23] for other metals. But further experiments are necessary to ascertain the role of proton incorporation on the electrochemical properties of the oxide film. At the oxide–solution interface, a complex forming reaction occurs according to:

$$Zr^{4+} + nHF \rightleftarrows ZrF_n^{(n-4)-} + n\,H^+ \quad (10)$$

The renewal of $Zr^{4+}$ ions at the oxide surface involves diffusion of $Zr^{4+}$ through the film according to the Mott–Cabrera theory.[20]

For Ti and Zr, Raman spectrometry shows that the fluoro-metal complexes formed during pickling may further react with $HNO_3$ and $H_2O$ in the bulk of the solution to form more stable complexes whose nature depends on aging time and on acid and metal concentrations. The nitric acid is thus important in the production of soluble oxofluoro species, and the concentration of metal ion at saturation of the pickling bath is raised. These oxofluoro species are dimeric or polymeric with Ti–O–Ti and Zr–O–Zr bridges.

## CONCLUSION

▶ During pickling of Ti and Zr in HF–$HNO_3$ solutions, hydrofluoric acid behaves like a complexing reagent towards both metals, but the role of $HNO_3$ is different in each case. It oxidizes $Ti^{III}$ to $Ti^{IV}$ either as soluble Ti fluorides or as insoluble Ti oxide, according to Equations (5) or (6) above. In the case of Zr, the role of nitric acid is simply to increase ($H^+$) and thus the film thickness. Nevertheless, $HNO_3$ acts as an oxidizer towards fluoro-metal complexes in both cases and favors the formation of oxofluorometal species with higher solubility in the pickling solution. Thus the total fluoride to metal molar ratio can reach a value 2 without precipitation.

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